

NO DRAWINGS

- (21) Application No. 12722/70 (22) Filed 17 March 1970
(31) Convention Application No. 809979 (32) Filed 24 March 1969 in
(33) United States of America (US)
(44) Complete Specification published 4 Jan. 1973
(51) International Classification C08F 7/04 1/02
(52) Index at acceptance

C3P 13D5A 13G2A 13G4A 13H1 13H3 13HX 13N3 13T1A
13T1C 13Y

C3G 1B2 1C1 2C 3A1 3C3

- (72) Inventor KENNETH LEO BURGESS



(54) POLYMER PREPARATION

(71) We, THE DOW CHEMICAL COMPANY, a Corporation organised and existing under the laws of the State of Delaware, United States of America, of Midland, County of Midland, State of Michigan, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to polymerization of styrene and more particularly relates to the preparation of styrene-type polymers employing a two step polymerization.

Styrene-type polymers have found wide commercial acceptance, such as polystyrene, rubber-modified impact polystyrene. Generally, such polymers are prepared by the polymerization of the monomer, often thermally; that is, by heat alone, or in the presence of a free radical-generating catalyst such as a peroxide or in the presence of anionic catalysts such as sodium, lithium or organolithium compounds such as butyllithium. In the mass polymerization of styrene-type polymers, the reaction is exothermic and substantial quantities of heat are removed from the polymerizing mass. Often, the polymerized material is usually treated in its heat plastified form to a devolatilizing step wherein minor amounts of unpolymerized monomer, dimers, trimers and solvent are removed. The devolatilized polymer is subsequently cooled and pelleted in and one of several manners to provide a moulding granule. Generally, such moulding granules are reheated to a temperature sufficient to heat plastify the mass and subsequently extruded, moulded or otherwise fabricated into a desired article. Various grades of polystyrene are available wherein the primary difference between them is one of molecular weight and molecular weight distribution. Styrene polymers are also available which contain reinforcing agents such as rubber in

varying amounts and also have varying molecular weight grades particularly suited to desired end uses or fabricating processes. As an indication of molecular weight, there is commonly employed a measurement referred to as "solution viscosity" which is the viscosity of a 10 weight percent solution of polystyrene and at least the soluble fraction of a rubber-reinforced styrene polymer in toluene at 25°C. Commonly available moulding grade polystyrenes vary in solution viscosity from about 15 to 35 centipoises. The solution viscosity is a general indication of the molecular weight but is not meaningful to determine the molecular weight distribution. For some applications, styrene polymer is desired having high molecular weight, having low molecular weight or having a broad or narrow molecular weight distribution. In order to prepare styrene polymers of varying characteristics, it is often necessary to radically alter the processing conditions, such as in a thermal polymerization process where, if high molecular weight material is desired, the temperature of polymerization is maintained at a lower temperature than if a low molecular weight material is desired. Generally, in order to obtain maximum production from a given polymerization system, it is desirable to polymerize as rapidly as possible which frequently means in a thermal polymerization that low molecular weight material is obtained. In large scale polymerization equipment, it is usually undesirable to alter operating conditions to vary the nature of the product. Often an intermediate material is obtained during the change of conditions which fails to meet the requirements of the material originally being produced and that which is desired to be produced. Generally in the preparation of styrene polymers by thermal polymerization or in the presence of a free radical promoter, activator or catalyst, the polymerization rate and volumetric efficiency of the reactor decreases rapidly with increasing conversion.

[Price 25p]

When 90 or 95 percent conversion of monomer to polymer is obtained, the rate of polymerization becomes low, frequently requiring large vessels heated to relatively high temperatures to complete the polymerization to a desired practical degree. Generally in such polymerizations, the mole fraction of monomer converted to polymer at a given instant is generally proportional to the mole fraction of monomer present. Rarely is it possible, although it is highly desirable, that the product of a polymerization reaction system be fed to a processing apparatus such as an extruder or moulding machine to produce desired articles and eliminate the need of cooling the polymer, granulating it, shipping the granules and subsequently reheating. The above deficiencies have been largely overcome by the present invention which is a method for preparing a prepolymer syrup which is a solution of a styrene polymer in its monomer, cooling the solution of polymer and monomer to a temperature sufficient to halt significant polymerization, subsequently inducing completion of the polymerization in the solution by mixing therewith an anionic polymerization promoter in sufficient quantity to cause the remaining monomer to polymerize to a desired molecular weight.

Polymerizations of a styrene monomer with anionic polymerization promoters or catalysts are well known, as is the control of molecular weight by varying the amount of the promoter. US Letters Patent 3,031,432 issued to Kern April 24, 1962, describes control of molecular weight using organolithium compounds. Such control is also described in "The Polymerization of Styrene by n-Butyllithium" by F. J. Welch, *Journal of the American Chemical Society*, Vol. 81, pages 1345—1348 (1959).

UK Patent Specification No. 1,174,845 relates to the polymerization of vinyl-aromatic compounds and describes a process for manufacturing a polyvinyl-aromatic compound in which a monomeric vinyl-aromatic compound as hereinbefore defined is polymerized with the aid of an anionic catalyst, wherein there is dissolved in said monomeric vinyl-aromatic compound at least 10% by weight of a substantially non-volatile additive which is inert with respect to said catalyst whereby at least a major proportion of the exothermic heat of polymerization is absorbed within the polymerization reaction mixture.

Many anionic polymerization promoters are known which are suitable for polymerization of monomers such as styrene; alkali metals such as lithium, sodium, potassium, rubidium, caesium; and alkali metal hydrocarbon compounds such as butyllithium, sodium naphthalene, cyclohexyllithium; alfin catalysts such as are described in US Patent 2,841,574, issued to Foster July 1, 1958; organometallic compounds such as are set

forth in US Patents 3,294,768, issued to Wofford December 27, 1966, 3,379,705, issued to Rothlisberger April 23, 1968, and 3,379,706, issued to Wilke April 23, 1968. Advantageously, suitable catalysts or promoters are those which initiate polymerization at relatively low temperatures; i.e. from about 0°C. to 60°C. Particularly beneficial are the alkyl-lithium catalysts, which readily initiate polymerization at temperatures of 20°C. to 40°C. and above. Removal or inactivation of such catalysts after polymerization is well known and described in the foregoing reference.

Beneficially, in the practice of the present invention, styrene-type monomers which are utilized are those that polymerize readily in the presence of an anionic promoter and in which the monomers and polymers of the monomers do not contain active hydrogen which reacts with the promoter to destroy its effectiveness as a polymerization inducing agent. Suitable styrene-type monomers are styrene, vinyl toluene, ethyl styrene, dodecyl styrene, octyl styrene, and butyl styrenes such as t-butylstyrene. Other monomers known to polymerize with styrene-type monomers in the presence of anionic catalysts may be employed e.g. methyl methacrylate. Such monomers may be employed either alone or in admixture with each other. Advantageously, the so-called impact styrene polymers are readily prepared wherein a rubber is incorporated in the monomer mixture and the monomer subsequently polymerized. Fillers, pigments and other additives also may be employed provided that such additives are inert with respect to the anionic catalyst present, or sufficient catalyst is provided for polymerization of the monomer and to react with other materials present which may preferentially react with the anionic catalyst.

In accordance with the present invention there is provided a method for preparing a styrene-type polymer comprising thermally polymerizing a styrene-type monomer to prepare a prepolymer syrup, the monomer containing no active hydrogen atoms; cooling the syrup to stop polymerization; determining the monomer content in the syrup; and polymerizing the remaining monomer in the syrup by adding an anionic polymerization promoter to the syrup and initiating polymerization at 35—40°C the heat of polymerization being employed to raise the temperature of the polymerized composition to a temperature at or above its thermoplastic temperature.

Preferably, the prepolymer syrup contains from 30 to 70 weight percent polymer, more preferably from 40 to 70 weight percent polymer.

Advantageously, a syrup of a desired polymer content is prepared by thermal polymerization, to give a solution containing about 60 weight percent polymer and having a given molecular weight. The prepolymer or syrup

can then be cooled, stored and/or transported. Beneficially, the prepolymer may be stored for extended periods such as days, weeks or even months, shipped over relatively long distances to storage facilities and/or the site of final polymerization and moulding or shaping. When heat-plastified polymer is desired, a predetermined quantity of anionic catalyst is added, with vigorous agitation, to the syrup, the quantity of anionic catalyst being calculated so that the remaining monomer will polymerize to a desired molecular weight whereby the final product consists of about 60 percent thermally polymerized polymer, about 40 percent anionic polymerized polymer, and the final product has the desired molecular weight distribution. For purposes of calculation, the heat of polymerization of styrene may be taken as 17 kilocalories per mole and a heat capacity of styrene as 32 calories per mole and polystyrene as 45 calories per mole. As the polymerization of the styrene-type monomers is readily initiated by an anionic promoter at temperatures of about 35°C. to 40°C. and the reaction is exothermic, the heat liberated by the polymerizing monomer is sufficient to raise the temperature of the polymerized mass to a convenient processing temperature; for example 200°C., which permits the reaction mixture to be devolatilized and subsequently directly processed without the need for the addition of large quantities of heat required to heat plastify solid polystyrene. If, for example, employing styrene-polystyrene syrup containing significantly in excess of 60 weight percent polystyrene, and a catalyst such as n-butyllithium, the initial temperature at which the lithium catalyst is added can be raised; or if higher temperatures are required, styrene may be added prior to or simultaneously with the inclusion of lithium catalyst, thereby increasing the heat liberated by the polymerization and causing the final polymerized reaction mixture to reach a higher temperature. If the styrene and catalyst are premixed, beneficially the mixture is maintained at low temperatures at which little or no polymerization occurs. Generally, the vessels in which the final polymerization occurs are thermally insulated to prevent substantial heat loss. If the mass of the vessel is large compared to the volume of polymer, then the heat capacity of the vessel is low relative to the heat capacity of the reaction mixture (as is the case when a tubular or continuous reactor is employed) and one generally may ignore the heat capacity of the vessel. Similarly, when employing a continuous process and the reactor is well insulated, reactor heat capacity can be ignored. When metal vessels are employed, particularly large vessels, it is often desirable to incorporate the heat capacity of the vessel when calculating the final temperature of the polymerized mixture. Beneficially, when starting a continuous

reactor, excess styrene may be employed to provide the heat necessary to assure a heat plastified polymer at the discharge and provide the heat necessary to raise the reactor to the desired operating temperature. The rate of polymerization employing anionic catalysts is sufficiently rapid that heat losses generally are minimal in a continuous reactor as well as in batch reactors.

Polymerization in accordance with the present invention is readily carried out either continuously or batch wise. In mixing the anionic promoter with the prepolymer syrup, vigorous agitation is usually desirable. Variation in mixing of the anionic promoter with the prepolymer syrup can effect the molecular weight of the product. If mixing time is long relative to polymerization time, a broader distribution of molecular weight is obtained. Thus, in general, the more vigorous the agitation, the narrower the molecular weight distribution.

The following examples illustrate the invention. All solution viscosities are viscosities of a 10 weight percent solution in toluene as measured at 25°C.

EXAMPLE 1

A polymerization apparatus is provided which consists of a monomer reservoir in communication with a metering pump and a heat exchanger which consists of a length of 1/4 inch (0.64 cm.) outside diameter aluminum tube having an internal volume of 50 ml. The tube is disposed within a jacket through which heated air is circulated. The aluminum tube terminates in a polymerization vessel having an internal volume of 1.5 litres and a length to diameter ratio of about 5:1. An agitator is disposed within the vessel and the vessel is provided with heat exchange tubes running therethrough. An inlet and discharge are disposed at opposite ends of the polymerization vessel. A receiver reservoir is connected to the discharge of the polymerization vessel and the interior of the reservoir is blanketed with nitrogen. This apparatus will be referred to as the prepolymer polymerizer. A second polymerization apparatus, which will be referred to as the final polymerizer, is provided. The final polymerizer consists of a heat exchanger of similar design and dimension to that employed in the prepolymer polymerizer. The heat exchanger is in communication with a high shear mixer having a free volume of 5 cc. The mixer discharges into a thermally insulated 1/4 inch (0.64 cm.) diameter polymerizing tube having a volume of 250 ml. Distilled styrene containing less than 0.3 weight percent ethylbenzene is placed in the monomer reservoir of the prepolymer polymerizer and the heat exchanger heated to provide an exit temperature of the styrene of 150°C. at a flow rate of 1500 grams per hour. The heat exchange on the agitated vessel is

adjusted to provide an internal temperature of the vessel of 157°C. The effluent or prepolymer syrup from the agitated vessel is immediately cooled to 30°C. and stored in the reservoir under nitrogen. A sample of the syrup removed from the reservoir is determined to be 60 weight percent polystyrene having a solution viscosity of 15 centipoises. The syrup from the foregoing preparation is pumped at a rate of 1500 grams per hour through the heat exchanger of the final polymerizer where it is heated to 40°C. Normal butyllithium is added at a rate of 0.602 gram per hour at the inlet of the high shear mixer, the butyllithium being supplied as a 20 weight percent solution in ethylbenzene. At the exit of the polymerizing tube, the temperature of the effluent is 208°C. The effluent contains 98.5 weight percent polystyrene which has a solution viscosity of 25 centipoises. The effluent from the polymerizing tube is devolatilized employing a thermally insulated vessel having an internal pressure of 23 mm. The effluent is spread out as a thin downwardly flowing layer on the wall of the vessel. The devolatilizer is intermittently discharged to the cavity of a compression mould and the resultant polystyrene is moulded without further heating.

EXAMPLE 2

The procedure of Example 1 is repeated with the exception that the butyllithium is employed as a solution in styrene (maintained at about 15°C.) and added to the high shear mixer at a rate of 0.605 gram per hour of butyllithium and 75 grams per hour styrene. At the exit or discharge end of the polymerizing tube the temperature is 227°C. The product is 99.1 weight percent polystyrene and has a solution viscosity of 25.8 centipoises.

EXAMPLE 3

The procedure of Example 1 is repeated with the exception that the shear rate in the high shear mixer is reduced to one half of the rate employed in Example 1. The product issuing from the polymerizing tube is 97.8 weight percent polystyrene and has a temperature of 203°C. and a solution viscosity of 23 centipoises. Comparison of the polymer product with that of Example 1 by means of gel permeation chromatography indicates that molecular weight range is substantially narrower with higher agitation.

EXAMPLE 4

The procedure of Example 1 is repeated with the exception that prior to entering the devolatilizer, one gram of water per hour is mixed with the effluent stream. The resultant polymer has less than 0.05 percent residual monomer, is transparent and non-yellowing. 7.5 Grams of finely divided titanium dioxide contained in 25 grams of polystyrene are

mixed with the effluent from the polymerizing tube and devolatilized. The product does not turn yellow on standing. When the water addition is omitted, the material from the polymerizing tube is discharged into a flask, air cooled and subsequently ground. The material yellows on standing.

EXAMPLE 5

The procedure of Example 4 is repeated with the exception that 6 grams per hour of stearic acid are added in place of water. A non-yellowing product is obtained having less haze than the polymer of Example 4.

EXAMPLE 6

Employing the apparatus of Example 1, the styrene feed rate to the prepolymer polymerizer is 1050 grams per hour. The preheater delivers a stream of styrene at 40°C. The temperature in the agitated reactor is maintained at 150°C. The reaction mixture from the prepolymerizer is 60 weight percent polystyrene. The polystyrene has a viscosity of 20.2 centipoises. A portion of the reaction mixture is passed to the final polymerizer which is maintained under conditions set forth in Example 1. The temperature of the product from the polymerizing tube is 207°C. and the product contains 98.3 percent polystyrene having a solution viscosity of 30 centipoises.

EXAMPLE 7

Employing the prepolymerizer and conditions of Example 1, with the exception that the feed rate of styrene is increased to 2000 grams per hour, a prepolymer syrup is obtained which is 50 weight percent polystyrene and the polystyrene has a solution viscosity of 14.8 centipoises. The prepolymer syrup is then passed to the final polymerizer at a rate of 1500 grams per hour at a temperature of 40°C. from the preheater. 0.753 Gram of n-butyllithium per hour is added as a 20 percent solution in ethylbenzene. The mixture issuing from the polymerizing tube has a polymer content of 98.8 weight percent polystyrene and a solution viscosity of 27.3 centipoises.

EXAMPLE 8

A solution of polybutadiene rubber, commercially available under the trade designation of "Diene 35", is dissolved in styrene to provide a 5 weight percent solution of the rubber in styrene. The solution is heated to 46°C. and placed under a pressure of 20 mm. of mercury absolute to separate trace amounts of water therefrom. The solution is passed through the prepolymerizer employing the conditions of Example 1 with the exception that the feed rate is 1600 grams per hour. The product is 59 weight percent polystyrene and is a heterogeneous, viscous mixture. The mixture is stored at 40°C. and a portion subse-

quently passed through the final polymerizer (employing the temperature of Example 1) at a rate of 1500 grams per hour wherein 0.602 gram per hour of butyllithium is added as a 20 percent solution in benzene. The material issuing from the polymerizing tube has a temperature of 206°C. The material is moulded and has a 0.75 foot-lb./inch (1.04×10^4 g.-cm./2.54 cm.). Izod impact strength and a 95° Vicate heat distortion temperature. The moulded specimens exhibit a glossy surface.

EXAMPLE 9

A portion of the prepolymer prepared in Example 8 containing polybutadiene rubber is passed to the final polymerizer wherein the heat exchanger is adjusted to provide an effluent temperature of 55°C. The catalyst employed is 0.310 gram per hour of finely divided sodium as a 10 percent dispersion in mineral oil. The dispersion has a particle size from below 1 micron to about 3 microns. The polymer discharge from the 1/4 litre tube is 97.2 percent solids and has a temperature of 204°C. The reaction mixture is devolatilized and treated with water to destroy residual sodium. The moulded material has an Izod notched impact of 0.62 foot lb./inch (0.86×10^4 g.-cm./2.54 cm.), and mouldings prepared therefrom show good reproduction of the mould surface.

WHAT WE CLAIM IS:—

1. A method for preparing a styrene-type polymer comprising thermally polymerizing a styrene-type monomer to prepare a prepolymer syrup, the monomer containing no active hydrogen atoms; cooling the syrup to stop polymerization; determining the monomer content in the syrup; and polymerizing the remaining monomer in the syrup by adding an anionic polymerization promoter to the syrup and initiating polymerization at 35—40°C the heat of polymerization being employed to raise the temperature of the polymerized composition to a temperature at or above its thermoplastic temperature.
2. A method as claimed in claim 1 wherein the polymerization of the styrene monomer in the prepolymer syrup is initiated by a butyllithium catalyst.
3. A method as claimed in claim 1 or claim 2 wherein the prepolymer syrup contains from 30 to 70 weight percent polymer.

4. A method as claimed in claim 1 or claim 2 wherein a prepolymer syrup contains from 40 to 70 weight percent polymer.

5. A method as claimed in any one of the preceding claims wherein after cooling the syrup to stop polymerization the syrup is maintained at a predetermined temperature.

6. A method as claimed in claim 5 wherein the predetermined temperature is from 30°C to 60°C.

7. A method as claimed in any one of the preceding claims and including the step of inactivating the anionic catalyst.

8. A method as claimed in any one of the preceding claims for the preparation of a styrene polymer having a desired solution viscosity, wherein the prepolymer syrup has contained there in a polystyrene of a known solution viscosity, and at least a major portion of the remaining monomer in the prepolymer syrup is polymerized to form a styrene polymer of a predetermined solution viscosity, the weighted average of the solution viscosities providing a mixture of polystyrene having the desired solution viscosity.

9. A method as claimed in any one of the preceding claims and including the step of devolatilizing the resultant heat-plastified mixture.

10. A method as claimed in any one of the preceding claims wherein homopolystyrene is prepared.

11. A method as claimed in any one of claims 1 to 9 wherein a rubber toughened styrene polymer is prepared.

12. A method as claimed in claim 1 and substantially as hereinbefore described with reference to the specific Examples.

13. A styrene polymer whenever prepared by a method as claimed in any one of the preceding claims.

14. A method as claimed in any one of claims 1 to 12 and including the step of subsequently forming at least a portion of the heat-plastified mixture into a shaped article.

15. A shaped article comprising styrene polymer as claimed in claim 13.

BOULT, WADE & TENNANT
Chartered Patent Agents
34 Cursitor Street London
EC4A 1PQ

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1973.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.